

PATENT SPECIFICATION

NO DRAWINGS

995,186



995,186

Date of Application and filing Complete Specification Aug. 19, 1963.

No. 3265/63.

Application made in Italy (No. 16773) on Aug. 22, 1962.

Complete Specification Published June 16, 1965.

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Index at acceptance: —Cl A(D16, G9, G10, G13, G21, G22, G34, G37, G38, G40, GX), AG9D16, AG10D16, AG13D16, AG21D16, AG22D16, AG34D16, AG37D16, AG38D16, AG40D16, AGXD16

Int. Cl.:—C 01 g

COMPLETE SPECIFICATION

Transition Metal Fluorides

We, MONTECANTI SOCIETA GENERALE PER L'INDUSTRIA MINERARIA E CHIMICA, a Body Corporate organised and existing under the laws of Italy, of 1—2, Largo Guido Donegani, Milan, Italy, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the preparation of transition metal fluorides, which includes mixed halides with chlorine or bromine, by a process which does not involve the use of fluorine or hydrofluoric acid as a reagent and all the difficulties attendant upon their corrosive and poisonous properties.

The invention provides a process of preparing transition metal fluorides of the general formula:



in which M is a transition metal, X is chlorine or bromine, Y is an electron donor, n is a whole number from zero to a number not higher than one half of the valency of M, m is a whole number, $m+n$ is equal to the valency of M, and p is zero or a multiple of 0.5, which comprises fluorinating a compound of the general formula $[MX_nY_p]$ in which M, X, Y and p have the above mentioned meanings and q is the valency of M with ethylidene difluoride ($CH_2CH_2F_2$) or boron trifluoride under anhydrous conditions in the presence of a chlorine containing organic diluent.

The process of the invention should be carried out at a temperature between 0° and 200°C, preferably between 20° and 150°C.

Ethylidene difluoride which is a stable, non poisonous and easily handled compound is particularly suitable since it exchanges both its fluorine atoms with other halogen atoms,

it allows, without using an excess over the equivalent a quantitative fluorination of the transition metal compound; and if a mixed fluoride halide is desired, the number of chlorine or bromine atoms exchanged depends strictly on the relative amount of ethylidene difluoride used.

Boron trifluoride also exchanges all its fluorine atoms with the compounds to be fluorinated and has the advantage of being transformed, during the exchange, into easily volatile compounds. It is possible to employ more than one of these fluorinating agents at one time.

The exchange reactions are preferably carried out in the presence of a diluent having a high vapour pressure at room temperature for example methyl chloride or ethyl chloride, but other chlorine containing aliphatic hydrocarbons for example n -propyl chloride can alternatively be used. The amount of the diluent used can be varied within wide limits. It is however advisable to use at least one mol of diluent per mol of transition metal halide and preferably from 5 to 50 mols of diluent per mol of transition metal halide to be fluorinated.

The preferred reaction temperature depends on the particular transition metal halide to be fluorinated and on the fluorinating agent used. Thus, if the transition metal halides to be fluorinated consist of liquid compounds easily soluble in the diluent and if the fluorinating agent consists of ethylidene fluoride, the exchange reactions can profitably be carried out at temperatures of about 60°C. If the transition metal chloride to be fluorinated on the other hand consist of solid compounds which are not easily soluble in the diluent or if boron trifluoride is used as the fluorinating agent, it is in general more advantageous

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to operate at temperatures of about 100—150°C.

In particular cases, in which under the aforescribed conditions fluorination does not occur, it can be useful previously to complex the transition metal halide to be fluorinated, with electron donor compounds, for example ethers or pyridine. The mol ratio of electron donor compound used with respect to the compound to be fluorinated can vary between 0.5:1 and 20:1. Mol ratios between 1:1 and 5:1 are preferably used.

Transition metal halides which can be fluorinated according to the invention are those of metals belonging to Groups IVB, VB, VIB and VIII of the Periodic Table according to Mendeleef. Particularly suitable are the halides of titanium, zirconium, vanadium, chromium, molybdenum, tungsten, iron, nickel and cobalt. As halides, either chlorides or bromides can be used but chlorides are more suitable due to the formation of exchange compounds which can be removed more easily. The halides of the aforementioned transition metals can be used in all the valency states of the metal therein contained. As non-limitative examples of the transition metal halides which can be fluorinated according to the process of the invention we may mention: titanium tetrachloride, titanium trichloride, titanium dichloride, titanium tetrabromide, zirconium tetrachloride, vanadium tetrachloride, vanadium trichloride, vanadium dichloride, vanadium tribromide, chromium trichloride, chromium dichloride, molybdenum pentachloride, molybdenum trichloride, tungsten hexachloride, iron trichloride, iron dichloride, nickel dichloride, cobalt dichloride, cobalt dibromide.

The number of halogen atoms exchanged with fluorine depends on the amount of fluorinating agent used. One or more halogen atoms can be exchanged until all the halogen atoms have been substituted by fluorine atoms.

The fluorinated compounds obtained according to the process of the invention have physical, chemical and catalytic properties clearly different from those of the fluorinated compounds obtained by conventional methods. The fluorinated compounds obtained according to the invention in almost all cases are solid substances even if the starting halides were liquid. The fluorinated compounds obtained according to the invention in which all halogen atoms have been substituted by fluorine, are generally much more stable in the air and moisture than the respective starting halides. In many cases the completely fluorinated compounds do not smoke in the air do not have a vigorous reaction with water and alcohols. Unlike many transition metal fluorides prepared according to known methods, they can be stored even for long periods in glass containers without etching

them. Under X-ray examination in many cases they appear to be highly crystalline. In many other cases on the other hand their crystallinity is weak or they are completely amorphous.

The fluorinated compounds which have been prepared according to the invention are characterized by a particular state of division which, unlike most transition metal fluorides facilitates their effective use as catalysts in the controlled polymerization of monomers containing an ether group and in their copolymerization with other unsaturated compounds. In many cases they give valuable polymers which could not be obtained with known catalysts. If fluorinated compounds particularly effective as catalysts in the polymerization of unsaturated monomers containing an oxygen atom are desired, it is advisable to substitute fluorine for all or at least one half of the halogen atoms.

The invention includes compounds obtained by the process of the invention.

The following Examples illustrate the invention:

EXAMPLE 1.

A 150 cc autoclave cooled to -78°C has its air content replaced by nitrogen and the following substances introduced:

70 cc of anhydrous ethyl chloride,
11.0 g (0.071 mols) of titanium trichloride (gamma form) previously washed with *n*-heptane,

4.7 g (0.071 mols) of ethylidene difluoride. The autoclave is closed and agitation is started while adjusting to the reaction temperature to 90°C . After 15 hours of reaction the whole is cooled to room temperature and all volatile compounds are evaporated off under reduced pressure. 8.2 g of a violet powder which smokes in humid air, is thus obtained, whose elementary analysis, shows a molar ratio $\text{Ti}:\text{Cl}:\text{F}=1:1.1:1.9$.

EXAMPLE 2.

A 150 cc autoclave cooled to -78°C has its air content replaced by nitrogen and the following substances introduced:

80 cc of anhydrous ethyl chloride,
19.3 g (0.10 mols) of vanadium tetrachloride and

6.6 g (0.10 mols) of ethylidene difluoride. The autoclave is closed and agitation is started while heating to 60°C . After 15 hours of reaction at 60°C the mixture is cooled to room temperature and all volatile compounds are evaporated off under reduced pressure. 14.8 g of maroon powder, are thus obtained, which in the air produces greenish smoke, and whose elementary analysis shows a molar ratio $\text{V}:\text{Cl}:\text{F}=1:2:1.9$.

EXAMPLE 3.

150 cc autoclave cooled to -78°C has

its air content replaced by nitrogen and the following substances introduced:

- 70 cc of anhydrous ethyl chloride
 12.0 g (0.078 mols) of titanium trichloride (gamma form) previously washed with *n*-heptane.

- 17.0 g (0.26 mols) of ethylidene difluoride. The autoclave is closed and agitation is started while heating to 110°C. After 15 hours of reaction at 110°C the mixture is cooled to room temperature and all volatile compounds are evaporated off under reduced pressure. 8.2 g of a hazel-brown powder, apparently stable in the air, are obtained. X-ray examination of the product shows weak crystallinity bands typical of titanium trifluoride but the product appears prevalingly amorphous and its elementary analysis shows a molar ratio Ti:F=1:3 and a chlorine content lower than 0.5% by eight.

EXAMPLE 4.

- A 150 cc autoclave cooled to -78°C has its air content completely replaced by nitrogen and the following substances are introduced.

- 80 cc of anhydrous ethyl chloride,
 38.6 g (0.20 mols) of vanadium tetrachloride,
 33 g (0.50 mols) of ethylidene difluoride. The autoclave is closed and agitation is started while heating to 60°C. After 15 hours of reaction at 60°C, the whole is cooled to room temperature and all volatile compounds are evaporated off under reduced pressure. 22.5 g of a light grey powder are obtained which are apparently stable in the air. X-ray examination shows the product to be completely amorphous. Elementary analysis shows a molar ratio V:F=1:3.9 while the chlorine content is lower than 1% by weight.

EXAMPLE 5.

- A 150 cc autoclave cooled to -78°C has its air content completely replaced by nitrogen and the following substances introduced:
 80 cc of anhydrous ethyl chloride,
 5.0 g (0.031 mols) of anhydrous ferric chloride,
 5.0 g (0.076 mols) of ethylidene difluoride. The autoclave is closed and agitation is started while heating to 70°C. After 15 hours of reaction at 70° the mixture is left to cool and the volatile products are evaporated under reduced pressure. 3.1 g of hygroscopic dark maroon powder, soluble in benzene, are thus obtained. X-ray examination shows it to be practically amorphous: elementary analysis shows a molar ratio Fe:F=1:3, while the chlorine content is lower than 1%.

EXAMPLE 6.

- A 150 cc autoclave cooled to -78°C has its air content completely replaced by nitrogen and the following substances introduced:
 80 cc of anhydrous ethyl chloride,
 8.2 g (0.03 mols) of molybdenum pentachloride
 4.1 g (0.06 mols) of boron trifluoride. The autoclave is closed and agitation is started while heating to 145°C. After 20 hours of reaction at 145°C the mixture is cooled and volatile products are evaporated off under reduced pressure. 6.6 g of a black powder, crystalline under X-ray examination are obtained: elementary analysis shows the presence of Mo, F and Cl in the ratio 1:5.1:0.8.

WHAT WE CLAIM IS:—

1. A process of preparing transition metal fluorides of the general formula:



- in which M is a transition metal, X is chlorine or bromine, Y is an electron donor, *n* is a whole number from zero to a number not higher than one half of the valency of M, *m* is a whole number, *m*+*n* is equal to the valency of M, and *p* is zero or a multiple of 0.5, which comprises fluorinating a compound of the general formula $[MX_n]Y_p$, in which M, X, Y and *p* have the above mentioned meanings and *q* is the valency of M with ethylidene difluoride (CH₂CHF₂) or boron trifluoride under anhydrous conditions in the presence of a chlorine containing organic diluent.

2. A process according to claim 1 in which the reaction is carried out between +20° and +150°C.

3. A process according to claim 1 or 2 in which the transition metal is titanium, vanadium, chromium, molybdenum, iron or cobalt.

4. A process according to any of the preceding claims in which the molar ratio of electron donor to MX_q is between 0.5:1 and 20:1.

5. A process according to claim 4 in which the said molar ratio is between 1:1 and 5:1.

6. A process according to claim 4 or 5, in which pyridine is the electron donor compound.

7. A process according to any of the preceding claims in which ethyl chloride is the diluent.

8. A process of preparing transition metal fluorides substantially as hereinbefore described in any of the Examples.

9. Transition metal fluorides prepared by
the process of any of the preceding claims.

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317 High Holborn,
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Leamington Spa: Printed for Her Majesty's Stationery Office by the Courier Press.—1965.
Published at The Patent Office, 25, Southampton Building, London, W.C.2, from which copies may be obtained